

EK902078841US

"Express Mail" label mailing number

1/10/02

Date of Deposit

JC07 Rec'd PCT/PTO 10 JAN 2002

Form PTO-1390
(REV 10-95)

U. S. Department of Commerce Patent and Trademark Office

ATTORNEY'S DOCKET NUMBER

HF/5-22049/A/PCT

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/031999

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

INTERNATIONAL APPLICATION NO.
PCT/EP 00/06420

INTERNATIONAL FILING DATE
July 6, 2000

PRIORITY DATE CLAIMED
July 14, 1999

TITLE OF INVENTION

Metal complexes of tripodal ligands

APPLICANT(S) FOR DO/EO/US

**Frank Bachmann, Josef Dannacher, Menno Hazenkamp, Gunther Schlingloff, Grit Richter, Helena Dbaly and
Rainer Hans Traber**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau. **(See attached Form PCT/IB/308)**
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English 35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included.

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ **A FIRST preliminary amendment.**
 - ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: **(See attached Form PCT/ISA/210)**

U.S. APPLICATION NO. (if known, see 37 CFR 1.67)

10/031999

INTERNATIONAL APPLICATION NO.

PCT/EP 00/06420

ATTORNEY'S DOCKET NUMBER

HF/5-22049/A/PCT

17. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492(a) (1)-(5)):**

Search Report has been prepared by the EPO or JPO \$890.00

International preliminary examination fee paid to USPTO (37 CFR 1.482)
..... \$710.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482)
but international search fee paid to USPTO (37 CFR 1.445(a)(2)). \$740.00

Neither international preliminary examination fee (37 CFR 1.482) nor
international search fee (37 CFR 1.445(a)(2)) paid to USPTO. \$1040.00

International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(2)-(4). \$100.00

CALCULATIONS PTO USE ONLY**ENTER APPROPRIATE BASIC FEE AMOUNT = \$890.00**

Surcharge of \$130.00 for furnishing the oath of declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	22 - 20 =	2	X \$18.00	\$36.00
Independent claims	3 - 3 =	0	X \$84.00	\$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$
TOTAL OF ABOVE CALCULATIONS =				\$926.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also
be filed (Note 37 CFR 1.9, 1.27, 1.28).

SUBTOTAL = \$926.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

TOTAL NATIONAL FEE = \$926.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

TOTAL FEES ENCLOSED = \$

Amount to be: refunded	\$
charged	\$926.00

- a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 03-1935 in the amount of **\$926.00** to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to
Deposit Account No. 03-1935. A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or
(b)) must be filed and granted to restore the application to pending status.**

PLEASE ASSOCIATE THE ATTACHED APPLICATION WITH **CUSTOMER NUMBER 000324** AND SEND ALL CORRESPONDENCE TO:

JoAnn Villamizar, Ciba Specialty Chemicals Corporation
Patent Department
540 White Plains Road
P.O. Box 2005
Tarrytown, NY 10591-9005
DATE: **JAN 10 2002**

SIGNATURE

Kevin T. Mansfield

NAME

Reg. No. 31,635

10/031999

531 Rec'd PCT/PT 10 JAN 2002

CASE HF/5-22049/A/PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE PCT NATIONAL STAGE APPLICATION OF
FRANK BACHMANN ET AL
INTERNATIONAL APPLICATION NO. PCT/EP 00/06420
FILED: JULY 6, 2000
FOR: METAL COMPLEXES OF TRIPODAL
LIGANDS
U.S. APPLICATION NO: UNASSIGNED
35 USC 371 DATE:

Group Art Unit: unassigned
Examiner: unassigned

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

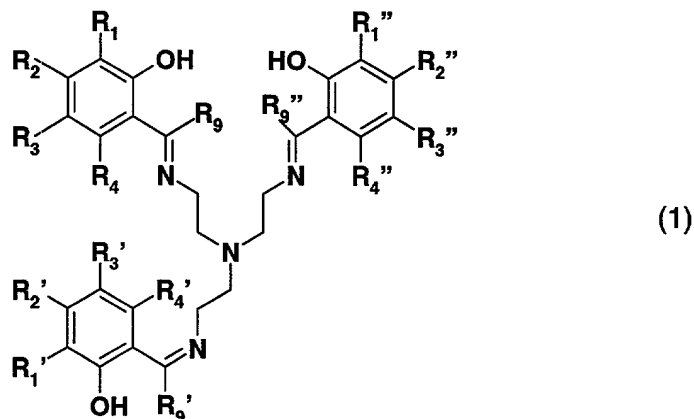
Kindly amend this application as follows prior to calculation of the filing fee and consideration on the merits.

IN THE CLAIMS

Please cancel claims 1-21.

Please add the following claims.

--22. **(new)** A process for oxidation, which comprises oxidizing an oxidizable substrate with a mixture of a peroxygen compound and, as oxidation catalyst, a metal complex containing a tripodal ligand of the formula

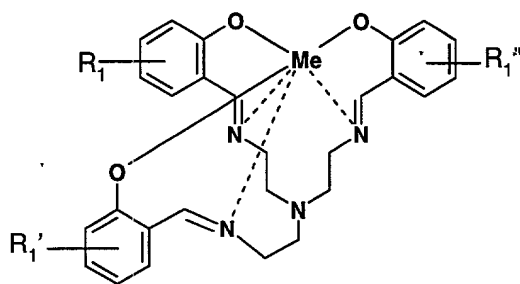


where

$R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3''$ and R_4'' are each independently hydrogen, cyano, halogen, SO_3M , where M is hydrogen, an alkali metal cation, an alkaline earth metal cation, ammonium or an organic ammonium cation, SO_2NH_2 , SO_2NHR_5 , $SO_2N(R_5)_2$, OR_5 or $COOR_5$, where R_5 is hydrogen or linear or branched C_1 - C_4 alkyl, nitro, linear or branched C_1 - C_8 alkyl, linear or branched fluorinated or perfluorinated C_1 - C_8 alkyl, NHR_6 , NR_6R_7 , $N^+R_6R_7R_{10}$ or linear or branched C_1 - C_8 alkyl- R_8 , where R_8 is OR_5 , $COOR_5$, NH_2 , NHR_6 , NR_6R_7 or $N^+R_6R_7R_{10}$, where R_6, R_7 and R_{10} are identical or different and each is linear or branched C_1 - C_{12} alkyl or where R_6 and R_7 combine with the joining nitrogen atom to form a 5-, 6- or 7-membered ring, which may contain further heteroatoms, and where R_9, R_9' and R_9'' are each independently hydrogen, linear or branched C_1 - C_8 alkyl or aryl.

23. **(new)** A process according to claim 22, in which the metal complex is an Mn(III) or Fe(III) complex containing a ligand of the formula (1).

24. **(new)** A process according to claim 23, in which the metal complex is a 1:1 metal(III) complex of the formula



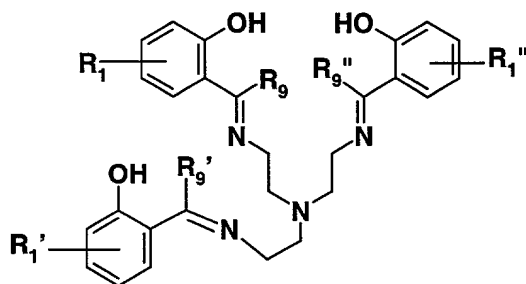
(2)

where Me is Mn or Fe, R_1 , R_1' and R_1'' are each independently hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxyl, nitro, NHR_6 , NR_6R_7 or $-N^{\oplus}R_5R_6R_7$, where R_5 , R_6 and R_7 are each independently C_1 - C_4 alkyl.

25. **(new)** A process according to claim 24, wherein the metal complex is an Mn(III) complex.

26. **(new)** A process according to claim 22, wherein a tripodal ligand of the formula (1) is used in an aqueous solution together with a peroxygen compound for bleaching spots or stains on textile material.

27. **(new)** A process according to claim 22, wherein the tripodal ligand conforms to the formula

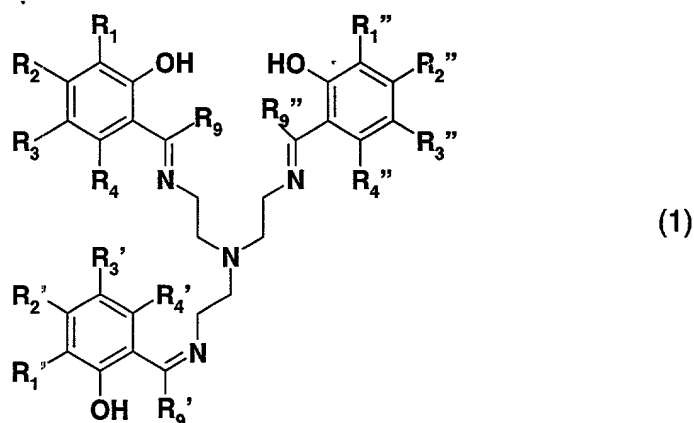


(3)

where

R_1 , R_1' and R_1'' are each independently hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxyl, nitro, NHR_6 , NR_6R_7 or $N^{\oplus}R_5R_6R_7$, where R_5 , R_6 and R_7 are each independently C_1 - C_4 alkyl and R_9 , R_9' and R_9'' are each independently hydrogen, linear or branched C_1 - C_8 alkyl or aryl.

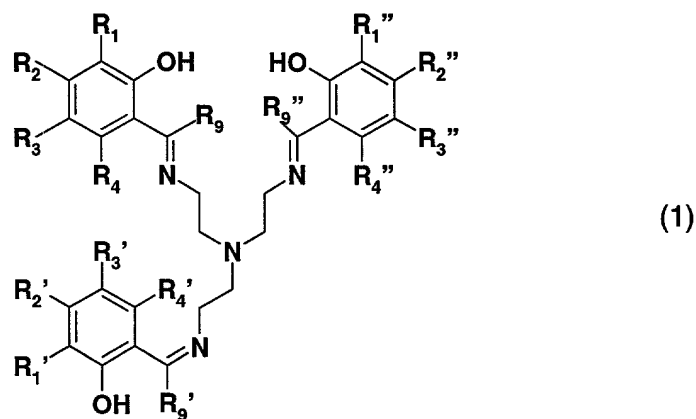
28. **(new)** A manganese(III) or iron(III) complex containing a tripodal ligand of the formula



where

$R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3''$ and R_4'' are each independently hydrogen, cyano, halogen, SO_3M , where M is hydrogen, an alkali metal cation, an alkaline earth metal cation, ammonium or an organic ammonium cation, SO_2NH_2 , SO_2NHR_5 , $SO_2N(R_5)_2$, OR_5 or $COOR_5$, where R_5 is hydrogen or linear or branched C_1 - C_4 alkyl, nitro, linear or branched C_1 - C_8 alkyl, linear or branched fluorinated or perfluorinated C_1 - C_8 alkyl, NHR_6 , NR_6R_7 , $N^{\oplus}R_6R_7R_{10}$ or linear or branched C_1 - C_8 alkyl- R_8 , where R_8 is OR_5 , $COOR_5$, NH_2 , NHR_6 , NR_6R_7 or $N^{\oplus}R_6R_7R_{10}$, where R_6, R_7 and R_{10} are identical or different and each is linear or branched C_1 - C_{12} alkyl or where R_6 and R_7 combine with the joining nitrogen atom to form a 5-, 6- or 7-membered ring, which may contain further heteroatoms, and where R_9, R_9' and R_9'' are each independently hydrogen, linear or branched C_1 - C_8 alkyl or aryl, subject to the condition that in the manganese(III) complex at least one of the substituents $R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3'', R_4'', R_9, R_9'$ and R_9'' has a meaning other than hydrogen and that at least one of the substituents R_3, R_3' and R_3'' has a meaning other than chlorine when the substituents $R_1, R_2, R_4, R_1', R_2', R_4', R_1'', R_2'', R_4'', R_9, R_9'$ and R_9'' are all hydrogen.

29. (new) A ligand of the formula



where

$R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3''$ and R_4'' are each independently hydrogen, cyano, halogen, SO_3M , where M is hydrogen, an alkali metal cation, an alkaline earth metal cation, ammonium or an organic ammonium cation, $SO_2NH_2, SO_2NHR_5, SO_2N(R_5)_2, OR_5$ or $COOR_5$, where R_5 is hydrogen or linear or branched C_1-C_4 alkyl, nitro, linear or branched C_1-C_8 alkyl, linear or branched fluorinated or perfluorinated C_1-C_8 alkyl, $NHR_6, NR_6R_7, N^{\oplus}R_6R_7R_{10}$ or linear or branched C_1-C_8 alkyl- R_8 , where R_8 is $OR_5, COOR_5, NH_2, NHR_6, NR_6R_7$ or $N^{\oplus}R_6R_7R_{10}$, where R_6, R_7 and R_{10} are identical or different and each is linear or branched C_1-C_{12} alkyl and where R_6 and R_7 combine with the joining nitrogen atom to form a 5-, 6- or 7-membered ring, which may contain further heteroatoms, or where R_9, R_9' and R_9'' are each independently hydrogen, linear or branched C_1-C_8 alkyl or aryl, subject to the condition that at least one of the substituents $R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3'', R_4'', R_9, R_9'$ and R_9'' has a meaning other than hydrogen and that at least one of the substituents R_3, R_3' and R_3'' has a meaning other than chlorine when the substituents $R_1, R_2, R_4, R_1', R_2', R_4', R_1'', R_2'', R_4'', R_9, R_9'$ and R_9'' are all hydrogen.

30. **(new)** A washing or cleaning process, which comprises adding to a liquor which contains a peroxidic detergent, 0.1 to 200 μ mol per litre of wash liquor of one or more metal complexes or an uncomplexed ligand of the formula (1) according to claim 29.

31. **(new)** A process for preventing the redeposition of migrating dyes in a wash liquor, which comprises adding to the wash liquor, which contains a peroxidic detergent, 0.5 to 150 mg per litre of wash liquor of one or more metal complexes containing a tripodal ligand of the formula (1) as defined in claim 22.

32. **(new)** A laundry detergent comprising

I) 5 - 90% of A) an anionic surfactant and/or B) a nonionic surfactant,

II) 5 - 70% of C) a builder,

III) 0.1 - 30% of D) a peroxide, and

IV) 0.005 - 2% of E) a metal complex containing a tripodal ligand of the formula (1) as defined in claim 22, the percentages all being percent by weight based on the total weight of the laundry detergent.

33. **(new)** A process according to claim 22, in which a hard surface is cleaned.

34. **(new)** A hard surface cleaner, which comprises a peroxygen compound and a metal complex containing a tripodal ligand of the formula (1) as defined in claim 22 as catalyst for the peroxygen compound.

35. **(new)** A hard surface cleaner according to claim 34, which is an automatic dishwasher cleaning composition.

36. **(new)** A process for cleaning crockery, which comprises using a hard surface cleaner according to claim 35.

37. **(new)** A process according to claim 33, wherein the hard surfaces which are cleaned are tiles and inter-tile joints.

38. **(new)** A process according to claim 22, which is a process for killing bacteria or for protecting a surface against bacterial colonization.

39. **(new)** An aqueous suspension comprising

- a) 1 - 60% by weight of a metal complex containing a tripodal ligand of the formula (1) as defined in claim 22,
- b) 0.5 to 15% by weight of a dispersant,
- c) 0 - 10% by weight of a further ingredient, and
- d) 15 - 98.5% by weight of water.

40. **(new)** A solid preparation comprising

- a) 1 - 99% by weight of a metal complex containing a tripodal ligand of the formula (1) as defined in claim 22,
- b) 1 to 99% by weight of a carrier material,
- c) 0 - 20% by weight of a dispersant,
- d) 0 - 10% by weight of a further ingredient, and
- e) 0 - 5% by weight of water.

41. **(new)** An aqueous suspension according to claim 39, wherein the metal complex containing a tripodal ligand of the formula (1) as defined therein has an average particle size of less than 20 μm .

42. (new) A solid preparation according to claim 40, wherein the metal complex containing a tripodal ligand of the formula (1) as defined therein has an average particle size of less than 20 μm .

43. (new) A process according to claim 22, which is a process for removing printing inks from printed waste paper (de-inking).---

REMARKS

Claims 22-43 have been added and are the only claims pending. The newly presented claims are supported by the original claims. Applicants note that in formula (3) in claim 27, R_2 , R_2' and R_2'' have been replaced by R_9 , R_9' and R_9'' to be consistent with the numbering in formula (1). No new matter has been added.

Applicants aver that the claims are now in proper form for examination. An Action on the merits of the claims is respectfully awaited.

Respectfully submitted,



Kevin T. Mansfield
Agent for Applicants
Reg. No. 31,635

Ciba Specialty Chemicals Corporation
Patent Department
540 White Plains Road
P.O. Box 2005
Tarrytown, NY 10591-9005
(914) 785-7127

KTM22049PA

JAN 10 2002

Metal complexes of tripodal ligands

The present invention relates to the use of metal complexes of tripodal ligands based on tris(2-aminoethyl)amine as catalysts which enhance the action of peroxygen compounds in washing, cleaning and disinfecting processes. The invention further relates to compositions of the metal complexes and peroxygen compounds used in such processes and to the novel metal complexes and ligands and also to processes for preparing them.

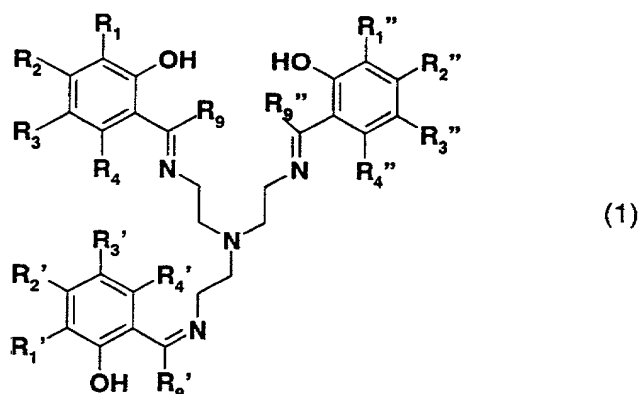
It is known that some manganese complexes, especially those of the salene type, are useful catalysts for oxidations with peroxygen compounds, especially as part of a washing processes. It is also known that certain other manganese complexes have a marked bleaching effect on dirt and dyes in wash liquors. There is nevertheless a demand for further compounds having an improved effect and/or having a broader application range, subject to the proviso that no significant fibre and dye damage may occur when applied to textile material.

It has now been found that certain metal complexes of tripodal ligands obtainable by reacting tris(2-aminoethyl)amine with aldehydes or ketones substantially meet the stated requirements when used as catalysts in that they enhance the action of peroxygen compounds in a wide variety of applications to a higher degree without occurrence of fibre and dye damage. Surprisingly, the enhanced effect occurs in applications including the following on using the metal complexes of such ligands in aqueous solution together with peroxygen compounds:

- a) bleaching spots or stains on textile material as part of a washing process,
- b) preventing the redeposition of migrating dyes during the washing of textile material,
- c) cleaning hard surfaces, especially crockery or glass,
- d) cleaning hard surfaces, especially tiles, particularly to remove mold stains,
- e) using washing and cleaning solutions having an antibacterial effect, and
- f) removing printing inks from printed wastepaper (de-inking).

The invention accordingly provides for the use of metal complexes containing a tripodal ligand of the formula

1003499-011002



where

$R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3''$ and R_4'' are each independently hydrogen, cyano, halogen, SO_3M , where M is hydrogen, an alkali metal cation, an alkaline earth metal cation, ammonium or an organic ammonium cation, SO_2NH_2 , SO_2NHR_5 , $SO_2N(R_5)_2$, OR_5 or $COOR_5$, where R_5 is hydrogen or linear or branched C_1 - C_4 alkyl, nitro, linear or branched C_1 - C_8 alkyl, linear or branched fluorinated or perfluorinated C_1 - C_8 alkyl, NHR_6 , NR_6R_7 , $N^+R_6R_7R_{10}$ or linear or branched C_1 - C_8 alkyl- R_8 , where R_8 is OR_5 , $COOR_5$, NH_2 , NHR_6 , NR_6R_7 or $N^+R_6R_7R_{10}$, where R_6, R_7 and R_{10} are identical or different and each is linear or branched C_1 - C_{12} alkyl or where R_6 and R_7 combine with the joining nitrogen atom to form a 5-, 6- or 7-membered ring, which may contain further heteroatoms, and where R_9, R_9' and R_9'' are each independently hydrogen, linear or branched C_1 - C_8 alkyl or aryl, as catalysts for oxidations with peroxygen compounds.

Particular preference is given to the use of Mn(III) and Fe(III) complexes containing a ligand of the above formula (1), especially an Mn(III) and Fe(III) complex which contains a ligand of the above formula (1) and metal in a molar ratio of 1:1.

Halogen is preferably chlorine, bromine or fluorine, particularly preferably chlorine.

Alkyl is particularly alkyl having 1 to 4 carbon atoms, especially methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl or tert-butyl.

R_6 and R_7 combining with the joining nitrogen atom to form a 5-, 6- or 7- ring are in particular a pyrrolidine, piperidine, morpholine or piperazine ring. The piperazine ring may be

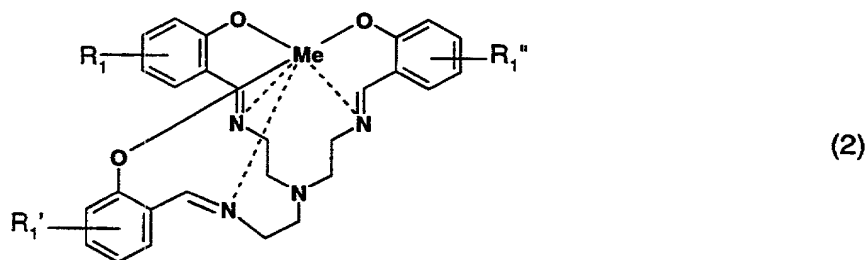
substituted, for example by alkyl, on the nitrogen atom not attached to the phenyl or alkyl radical.

Aryl is for example naphthyl or particularly phenyl.

R_9 , R_9' and R_9'' are each preferably independently hydrogen or C_1 - C_4 alkyl, especially hydrogen.

An alkali cation M in the SO_3M radicals may be for example lithium, potassium or particularly sodium, an alkaline earth metal cation M is selected in particular from magnesium and calcium.

Very particular preference is given to the use of the 1:1 Me(III) complexes of the formula



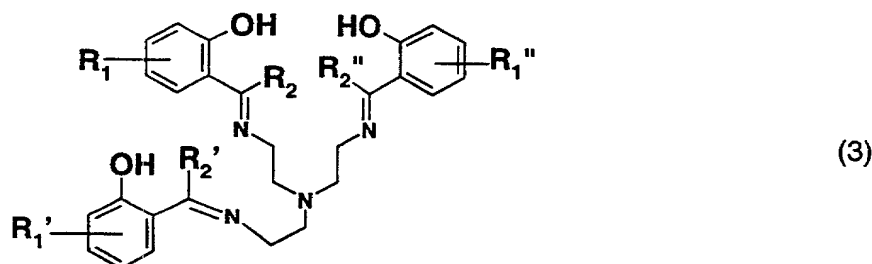
where Me is Mn or Fe, R_1 , R_1' and R_1'' are each independently hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxyl, nitro, NHR_5 , NR_5R_7 or $-N^+R_5R_6R_7$, where R_5 , R_6 and R_7 are each independently C_1 - C_4 alkyl, as catalysts for oxidations with peroxygen compounds.

Me in the formula (2) is preferably manganese.

The metal complexes containing a tripodal ligand of the formula (1) are preferably used in aqueous solution together with peroxygen compounds for bleaching spots or stains on textile material or for preventing the redeposition of migrating dyes as part of a washing process, or for cleaning hard surfaces, especially crockery or glass.

The ligands of the formula (1) are also useful in the uncomplexed form, as catalysts in aqueous solution with peroxygen compounds for bleaching spots or stains on textile material.

Preference for this use is given to the ligands of the formula

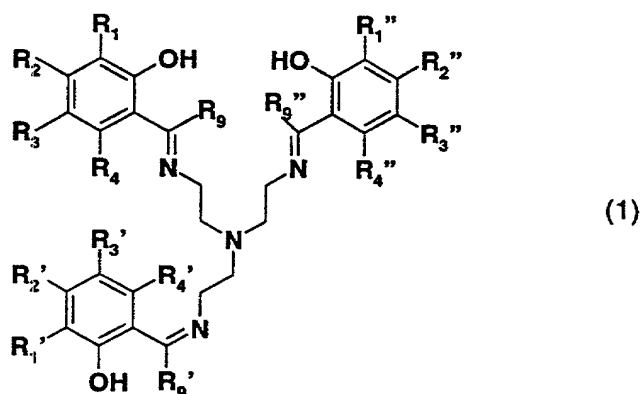


where

R_1 , R_1' and R_1'' are each independently hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxyl, nitro, NHR_6 , NR_6R_7 or $N^{\oplus}R_5R_6R_7$, where R_5 , R_6 and R_7 are each independently C_1 - C_4 alkyl and R_2 , R_2' and R_2'' are each independently hydrogen, linear or branched C_1 - C_8 alkyl or aryl.

Individual metal complexes containing a tripodal ligand of the formula (1) are already known, for example from S. Chandra, P. Chakraborty, A. Chakravorty, J. Chem. Soc., Dalton Trans. (1993), 6, 863.

Novel metal complexes are the manganese(III) and iron(III) complexes containing a tripodal ligand of the formula



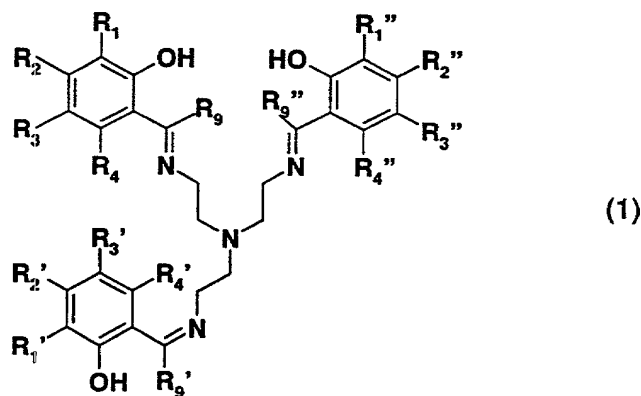
where

R_1 , R_2 , R_3 , R_4 , R_1' , R_2' , R_3' , R_4' , R_1'' , R_2'' , R_3'' and R_4'' are each independently hydrogen, cyano, halogen, SO_3M , where M is hydrogen, sodium, calcium, magnesium, ammonium or an organic ammonium cation, SO_2NH_2 , SO_2NHR_5 , $SO_2N(R_5)_2$, OR_5 or $COOR_5$, where R_5 is hydrogen or linear or branched C_1 - C_4 alkyl, nitro, linear or branched C_1 - C_8 alkyl, linear or

branched fluorinated or perfluorinated C₁-C₈alkyl, NHR₆, NR₆R₇, N[⊕]R₆R₇R₁₀ or linear or branched C₁-C₈alkyl-R₈, where R₈ is OR₅, COOR₅, NH₂, NHR₆, NR₆R₇ or N[⊕]R₆R₇R₁₀, where R₆, R₇ and R₁₀ are identical or different and each is linear or branched C₁-C₁₂alkyl or where R₆ and R₇ combine with the joining nitrogen atom to form a 5-, 6- or 7-membered ring, which may contain further heteroatoms, and where R₉, R₉' and R₉" are each independently hydrogen, linear or branched C₁-C₈alkyl or aryl, subject to the condition that in the manganese(III) complex at least one of the substituents R₁, R₂, R₃, R₄, R₁', R₂', R₃', R₄', R₁", R₂", R₃", R₄", R₉, R₉' and R₉" has a meaning other than hydrogen and that at least one of the substituents R₃, R₃' and R₃" has a meaning other than chlorine when the substituents R₁, R₂, R₄, R₁', R₂', R₄', R₁", R₂", R₄", R₉, R₉' and R₉" are all hydrogen.

These manganese(III) and iron(III) complexes also form part of the subject-matter of the present invention. They are obtained in a conventional manner by reacting a ligand of the formula (1) with a manganese or iron compound to form the corresponding metal complex. Such methods of operation are described for example in U.S. Pat. No. 5,281,578 and No. 4,066,459.

Also new are the ligands of the formula



where

R₁, R₂, R₃, R₄, R₁', R₂', R₃', R₄', R₁", R₂", R₃" and R₄" are each independently hydrogen, cyano, halogen, SO₃M, where M is hydrogen, an alkali metal cation, an alkaline earth metal cation, ammonium or an organic ammonium cation, SO₂NH₂, SO₂NHR₅, SO₂N(R₅)₂, OR₅ or COOR₅, where R₅ is hydrogen or linear or branched C₁-C₄alkyl, nitro, linear or branched C₁-C₈alkyl, linear or branched fluorinated or perfluorinated C₁-C₈alkyl, NHR₆, NR₆R₇, N[⊕]R₆R₇R₁₀ or linear or branched C₁-C₈alkyl-R₈, where R₈ is OR₅, COOR₅, NH₂, NHR₆, NR₆R₇

or $N^{\oplus}R_6R_7R_{10}$, where R_6 , R_7 and R_{10} are identical or different and each is linear or branched C_1 - C_{12} alkyl or where R_6 and R_7 combine with the joining nitrogen atom to form a 5-, 6- or 7-membered ring, which may contain further heteroatoms, and where R_9 , R_9' and R_9'' are each independently hydrogen, linear or branched C_1 - C_8 alkyl or aryl, subject to the condition that at least one of the substituents R_1 , R_2 , R_3 , R_4 , R_1' , R_2' , R_3' , R_4' , R_1'' , R_2'' , R_3'' , R_4'' , R_9 , R_9' and R_9'' has a meaning other than hydrogen and that at least one of the substituents R_3 , R_3' and R_3'' has a meaning other than chlorine when the substituents R_1 , R_2 , R_4 , R_1' , R_2' , R_4' , R_1'' , R_2'' , R_4'' , R_9 , R_9' and R_9'' are all hydrogen.

These ligands likewise form part of the subject-matter of the present invention. They are obtained in a conventional manner, for example by reacting tris(2-aminoethyl)amine with 3 mol of the substituted or unsubstituted salicylaldehyde. Reacting stepwise with three different salicylaldehydes or with mixtures of two or three different salicylaldehydes provides ligands of the formula (1) where the three aromatic rings have different substituents.

The metal complexes containing a tripodal ligand of formula (1) may before their use be converted into a solid or liquid preparation comprising the metal complex containing a tripodal ligand of the formula (1), a dispersant and optionally further ingredients and water.

It is advisable to grind the metal complexes, preferably to an average particle size of less than 20 μm , especially between 0.1 and 15 μm . Grinding may be effected together with the dispersants and further ingredients in dry form, but wet grinding is preferred. Grinding is effected in a conventional manner and in customary mills. The dry preparations obtained may be used in this form or may be slurried up in a solvent or water and used in the form of a suspension. Suspensions obtained from wet grinding may be used as such or may be dried and used in the form of solid preparations.

The present invention accordingly further provides aqueous suspensions comprising

- a) 1 - 60% by weight, preferably 5 - 30% by weight, of a metal complex containing a tripodal ligand of the formula (1),
- b) 0.5 to 15% by weight, preferably 1 - 5% by weight, of a dispersant,
- c) 0 - 10% by weight of a further ingredient, and
- d) 15 - 98.5% by weight of water.

The present invention further provides solid preparations comprising

- a) 1 - 99% by weight, preferably 5 - 50% by weight, of a metal complex containing a tripodal ligand of the formula (1),
- b) 1 to 99% by weight, preferably 50 - 95% by weight, of a carrier material,
- c) 0 - 20% by weight of a dispersant,
- d) 0 - 10% by weight of a further ingredient, and
- e) 0 - 5% by weight of water.

Useful dispersants include in particular anionic dispersants and nonionic dispersants.

The anionic dispersants used include for example commercially available water-soluble anionic dispersants for dyes, pigments, etc. Useful products include in particular: condensation products of aromatic sulfonic acid and formaldehyde, condensation products of aromatic sulfonic acids with possibly chlorinated biphenyls or diphenyl oxides and optionally formaldehyde, (mono/di-)alkylnaphthalenesulfonates, sodium salts of polymerized organic sulfonic acids, sodium salts of polymerized alkylnaphthalenesulfonic acid, sodium salts of polymerized alkylbenzenesulfonic acid, alkylarylsulfonates, sodium salts of alkylpolyglycol ether sulfates, polyalkylated polynuclear arylsulfonates, methylene-linked condensation products of arylsulfonic acids and hydroxyarylsulfonic acids, sodium salts of dialkylsulfosuccinic acid, sodium salts of alkyldiglycol ether sulfates, sodium salts of polynaphthalenemethanesulfonates, lignin- or oxygigninsulfonates or heterocyclic polysulfonic acids.

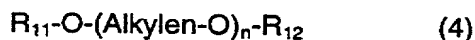
Particularly useful anionic dispersants are condensation products of naphthalenesulfonic acids with formaldehyde, sodium salts of polymerized organic sulfonic acids, (mono/di-)alkylnaphthalenesulfonates, polyalkylated polynuclear arylsulfonates, sodium salts of polymerized alkylbenzenesulfonic acid, ligninsulfonates, oxygigninsulfonates and condensation products of naphthalenesulfonic acid with the polychloromethylbiphenyl.

Useful nonionic dispersants include in particular water-emulsifiable, -dispersible or -soluble compounds having a melting point of at least 35°C. The following compounds are concerned, for example:

1. fatty alcohols having 8 to 22 carbon atoms, especially cetyl alcohol,

2. addition products of preferably 2 to 80 mol of alkylene oxide, especially ethylene oxide, in which case individual ethylene oxide units may be replaced by substituted epoxides, such as styrene oxide and/or propylene oxide, with higher saturated or unsaturated monoalcohols, fatty acids, fatty amines or fatty amides of 8 to 22 carbon atoms or with benzyl alcohols, phenylphenols, benzylphenols or alkylphenols whose alkyl radicals have at least 4 carbon atoms,
3. alkylene oxide, especially propylene oxide condensation products (block polymers),
4. ethylene oxide-propylene oxide adducts with diamines, especially ethylenediamine,
5. reaction products of fatty acid of 8 to 22 carbon atoms and a primary or secondary amine having at least one hydroxyloweralkyl or loweralkylloweralkyl group, or alkylene oxide addition products of these hydroxyalkyl-containing reaction products,
6. sorbitan esters, preferably having long-chain ester groups, or ethoxylated sorbitan esters, for example polyoxyethylene sorbitan monolaurate having 4 to 10 ethylene oxide units or polyoxyethylene sorbitan trioleate having 4 to 20 ethylene oxide units,
7. addition products of propylene oxide with a tri- to hexahydric aliphatic alcohol of 3 to 6 carbon atoms, for example glycerol or pentaerythritol, and
8. fatty alcohol polyglycol mixed ethers, especially addition products of 3 to 30 mol of ethylene oxide and 3 to 30 mol of propylene oxide with aliphatic monoalcohols of 8 to 22 carbon atoms.

Particularly useful nonionic dispersants are surfactants of the formula



where

R_{11} is C_8 - C_{22} alkyl or C_8 - C_{18} alkenyl;

R_{12} is hydrogen, C_1 - C_4 alkyl; a cycloaliphatic radical having at least 6 carbon atoms or benzyl;

"Alkylene" is an alkylene radical of 2 to 4 carbon atoms, and

n is from 1 to 60.

The substituents R_{11} and R_{12} in the formula (4) are advantageously the hydrocarbon radical of an unsaturated or preferably saturated aliphatic monoalcohol of 8 to 22 carbon atoms.

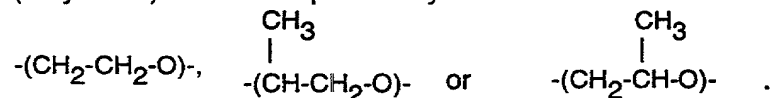
The hydrocarbon radical may be straight-chain or branched. Preferably R_{11} and R_{12} are each independently an alkyl radical of 9 to 14 carbon atoms.

Useful aliphatic saturated monoalcohols include natural alcohols, for example lauryl alcohol, myristyl alcohol, cetyl alcohol or stearyl alcohol, and also synthetic alcohols, for example 2-ethylhexanol, 1,1,3,3-tetramethylbutanol, octan-2-ol, isononyl alcohol, trimethylhexanol, trimethylnonyl alcohol, decanol, C₉-C₁₁ oxo alcohol, tridecyl alcohol, isotridecyl alcohol or linear primary alcohols (AlfolsTM) having 8 to 22 carbon atoms. Some representatives of these Alfols are Alfol (8-10), Alfol (9-11), Alfol (10-14), Alfol (12-13) or Alfol (16-18).

Examples of unsaturated aliphatic monoalcohols are dodecenyl alcohol, hexadecenyl alcohol and oleyl alcohol.

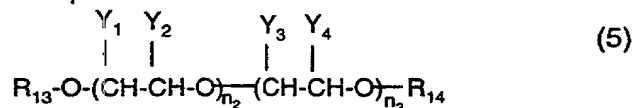
The alcohol radicals may be present individually or in the form of mixtures of two or more components, for example as mixtures of alkyl and/or alkenyl groups derived from soybean fatty acids, palm kernel fatty acids or tallow oils.

(Alkylen-O) chains are preferably divalent radicals of the formulae



Examples of a cycloaliphatic radical are cycloheptyl, cyclooctyl or preferably cyclohexyl.

Preferred nonionic dispersants are surfactants of the formula



where

R₁₃ is C₈-C₂₂alkyl;

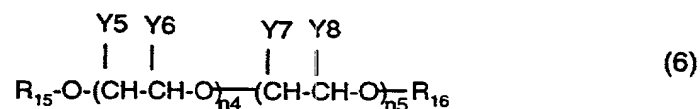
R₁₄ is hydrogen or C₁-C₄alkyl;

Y₁, Y₂, Y₃ and Y₄, are independently hydrogen, methyl or ethyl;

n₂ is from 0 to 8; and

n₃ is from 2 to 40.

Further important nonionic dispersants conform to the formula



where

R_{15} is C_9 - C_{14} alkyl;

R_{16} is C_1 - C_4 alkyl;

Y_5 , Y_6 , Y_7 and Y_8 , are independently hydrogen, methyl or ethyl, subject to the proviso that one of Y_5 , Y_6 on the one hand or Y_7 and Y_8 on the other is always hydrogen; and

n_4 and n_5 , are independently an integer from 4 to 8.

The nonionic dispersants of the formulae (4) to (6) may be used as mixtures. Useful surfactant mixtures accordingly include for example non-end-group-capped fatty alcohol ethoxylates of the formula (4), ie. compounds of the formula (4) where

R_{11} is C_8 - C_{22} alkyl,

R_{12} is hydrogen and

the Alkylen-O chain is the radical $-(CH_2-CH_2-O)-$,

and also end-group-capped fatty alcohol ethoxylates of the formula (6).

Examples of the nonionic dispersants of the formulae (4), (5) or (6) are reaction products of a C_{10} - C_{13} fatty alcohol, for example of a C_{13} oxo alcohol, with 3 to 10 mol of ethylene oxide, propylene oxide and/or butylene oxide, or the reaction product of one mole of a C_{13} fatty alcohol with 6 mol of ethylene oxide and 1 mol of butylene oxide. The addition products may each be end-group-capped by C_1 - C_4 alkyl, preferably methyl or butyl.

These dispersants may be used individually or as mixtures of two or more dispersants.

Useful carrier materials include for example: solid inorganic compounds possessing little if any hygroscopicity that are compatible with laundry detergent ingredients and are soluble or readily suspendible in water. Examples are oxides, such as MgO , CaO , TiO_2 , ZnO , Al_2O_3 and SiO_2 , especially Al_2O_3 and SiO_2 ; borates, aluminates, silicates, carbonates, phosphates, sulfates and aluminosilicates (zeolites) of alkali and alkaline earth metals, especially of sodium and of potassium. The oxo anions in these compounds may be linked via oxygen atoms to form larger chains, rings, layers or three-dimensional networks.

Examples of further ingredients include wetting agents, water-insoluble or water-soluble dyes or pigments and also fillers and optical brighteners. These ingredients are present in an amount of 0 to 10% by weight, based on the total weight of the solid or liquid preparation.

The metal complexes containing a tripodal ligand of the formula (1) are used as catalysts for oxidations with peroxygen compounds, for example for bleaching textile material, without causing significant damage to fibres and dyeings.

The present invention accordingly further provides a washing or cleaning process, which comprises adding to the liquor, which contains a peroxidic detergent, 0.1 to 200 μmol per litre of wash liquor of one or more metal complexes containing a tripodal ligand of the formula (1).

The present invention further provides a process for preventing the redeposition of migrating dyes in a wash liquor, which comprises adding to the wash liquor, which contains a peroxidic detergent, 0.5 to 150, preferably 1.5 to 75, especially 7.5 to 40, mg per litre of wash liquor of one or more metal complexes containing a tripodal ligand of the formula (1).

The present invention also provides a laundry detergent comprising

- I) 5 - 90%, preferably 5 - 70%, of A) an anionic surfactant and/or B) a nonionic surfactant,
- II) 5 - 70%, preferably 5 - 50%, especially 5 - 40%, of C) a builder,
- III) 0.1 - 30%, preferably 1 - 12%, of D) a peroxide, and
- IV) 0.005 - 2%, preferably 0.02 - 1%, especially 0.1 - 0.5%, of E) a metal complex containing a tripodal ligand of the above-defined formula (1), the percentages all being percent by weight based on the total weight of the laundry detergent.

The laundry detergent may be in solid or liquid form, for example in the form of a liquid nonaqueous composition including not more than 5%, preferably from 0 to 1%, by weight of water, and be based on a suspension of a builder in a nonionic surfactant, as described for example in GB-A-2,158,454.

Preferably, however, the laundry detergent is powdered or granular.

A powdered laundry detergent may be produced for example by first producing a starting powder by spray drying an aqueous slurry containing all above-recited components except components D) and E) and then adding the dry components D) and E) and mixing everything together.

It is also possible to add component E) to an aqueous slurry containing components A), B) and C), then to spray dry and subsequently to mix component D) with the dry material.

It is also possible to start with an aqueous slurry which contains component A) and C), but component B) either not at all or only in part. The slurry is spray dried, then component E) is mixed with component B) and added, and subsequently component D) is mixed in dry.

The anionic surfactant A) can be for example a sulfate, sulfonate or carboxylate surfactant or a mixture thereof.

Preferred sulfates are sulfates having 12 - 22 carbon atoms in the alkyl radical, optionally in combination with alkyl ethoxy sulfates whose alkyl radical possesses 10 - 20 carbon atoms.

Examples of preferred sulfonates are alkylbenzenesulfonates having 9 - 15 carbon atoms in the alkyl radical.

The cation in the anionic surfactants is preferably an alkali metal cation, especially sodium.

Preferred carboxylates are alkali metal sarcosinates of the formula $R-CO-N(R^1)-CH_2COOM^1$, where R is alkyl or alkenyl having 8 - 18 carbon atoms in the alkyl or alkenyl radical, R^1 is C_1-C_4 alkyl and M^1 is an alkali metal.

The nonionic surfactant B) can be for example a condensation product of 3 - 8 mol of ethylene oxide with 1 mol of primary alcohol having 9 - 15 carbon atoms.

Builder C) may be for example alkali metal phosphate, especially tripolyphosphate, carbonate or bicarbonate, especially the sodium salt thereof, silicate, aluminosilicate, polycarboxylate, polycarboxylic acid, organic phosphonate, aminoalkylene-poly(alkylenephosphonate) or a mixture thereof.

Particularly useful silicates are sodium salts of crystalline sheet-silicates of the formula $NaHSi_tO_{2t+1} \cdot pH_2O$ or $Na_2Si_tO_{2t+1} \cdot pH_2O$, where t is between 1.9 and 4 and p is between 0 and 20.

Preferred aluminosilicates are those commercially available under the name zeolite A, B, X and HS and also mixtures comprising two or more of these components.

Preferred polycarboxylates are polyhydroxycarboxylates, especially citrates, and acrylates and also copolymers thereof with maleic anhydride.

Preferred polycarboxylic acids are nitrilotriacetic acid, ethylenediaminetetraacetic acid and also ethylenediaminedisuccinate not only in racemic form but also as the enantiomerically pure S,S-form.

Particularly useful phosphonates or aminoalkylenepoly(alkylenephosphonate)s are alkali metal salts of 1-hydroxyethane-1,1-diphosphonic acid, nitrilotris(methylenephosphonic acid), ethylenediaminetetramethylenephosphonic acid and diethylenetriaminepenta-methylenephosphonic acid.

Peroxide component D) may be selected for example from the literature-described and commercially available organic and inorganic peroxides which bleach textile materials at customary washing temperatures, for example at 10 to 95°C.

The organic peroxides concerned are for example mono- or polyperoxides, especially organic peracids or salts thereof, such as phthalimidoporexycaproic acid, peroxybenzoic acid, diperoxydodecanedioic acid, diperoxynonanedioic acid, diperoxydecanedioic acid, diperoxyphthalic acid or salts thereof.

Preferably, however, inorganic peroxides are used, for example persulfates, perborates, percarbonates and/or persilicates. It will be appreciated that mixtures of organic and/or inorganic peroxides may be used as well. The peroxides may be present in different crystal forms and with different water contents and they may also be used together with other organic or inorganic compounds to improve their stability in storage.

The peroxides are preferably incorporated into the laundry detergent by mixing of the components, for example by means of a screw metering system and/or a moving bed mixer.

In addition to the combination of the invention, the laundry detergents may include one or more optical brighteners, for example from the group consisting of bistriazinylamino-stilbenedisulfonic acid, bistriazolylstilbenedisulfonic acid, bisstyrylbiphenyl, bisbenzofuranyl-biphenyl, a bisbenzoxalyl derivative, a bisbenzimidazolyl derivative, a coumarin derivative and a pyrazoline derivative.

The laundry detergent may further include soil suspenders, for example sodium carboxymethylcellulose, pH regulators, for example alkali or alkaline earth metal silicates, foam regulators, for example soap, salts for controlling the spray drying and the granulating properties, for example sodium sulfate, scents and also optionally antistats, fabric conditioners, enzymes, such as amylase, bleaching agents, pigments and/or shading agents. It will be appreciated that these ingredients have to be stable with regard to the bleaching agent used.

Further preferred ingredients of the laundry detergents according to the invention are polymers to inhibit textiles that are being washed from being tainted by dyes in the wash liquor that have become detached from the textiles under the conditions of the wash. These polymers are preferably polyvinylpyrrolidones or polyvinylpyridine N-oxides, optionally modified through incorporation of anionic or cationic substituents, especially such polymers having a molecular weight in the range from 5000 to 60,000, especially from 10,000 to 50,000. These polymers are preferably used in an amount of 0.05 to 5% by weight, especially 0.2 to 1.7% by weight, based on the total weight of the laundry detergent.

The laundry detergents of the invention may additionally include perborate activators, for example TAED, TAGU or SNOBS. Preference is given to TAED, which is preferably used in an amount of 0.05 to 5% by weight, especially 0.2 to 1.7% by weight, based on the total weight of the laundry detergent.

Surprisingly, metal complexes containing a tripodal ligand of the formula (1) also have a significantly improved bleach-catalysing effect on coloured stains on hard surfaces. A dishwashing composition that includes these complexes in catalytic amounts as well as a peroxygen compound with or without TAED (N,N,N',N'-tetraacetythylenediamine) will substantially remove tea stains on porcelain at 45°C in the dishwasher. This holds even for

the use of hard water, in which the removal of tea stains is known to be more difficult to achieve than in soft water.

The present invention accordingly further provides for the use of metal complexes containing a tripodal ligand of the formula (1) as catalysts for reactions with peroxy compounds in cleaning solutions for hard surfaces, especially for crockery.

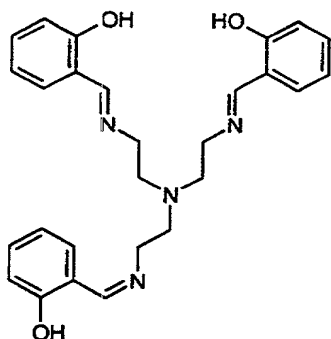
The present invention further provides a hard surface cleaner, especially a cleaner for crockery, a crockery cleaner for use in machine cleaning processes, comprising one of the metal complexes described above containing a tripodal ligand of the formula (1) as a bleach catalyst, and a process for cleaning hard surfaces, especially crockery, using such a bleach catalyst.

The inventive metal complexes containing a tripodal ligand of the formula (1) are also very useful for cleaning hard surfaces, especially tiles, particularly for removing mold stains. Such stains frequently occur especially in the joints between the tiles. These joints may be for example in cementitious and/or gypseous material or in polymer, for example silicone.

The invention accordingly further provides for the use of metal complexes containing a tripodal ligand of the formula (1) as catalysts for reactions with peroxygen compounds in cleaning solutions for tiles and inter-tile joints, and the cleaning solutions used for this purpose that include a metal complex containing a tripodal ligand of the formula (1) and a peroxide with or without further ingredients such as, for example, surfactants.

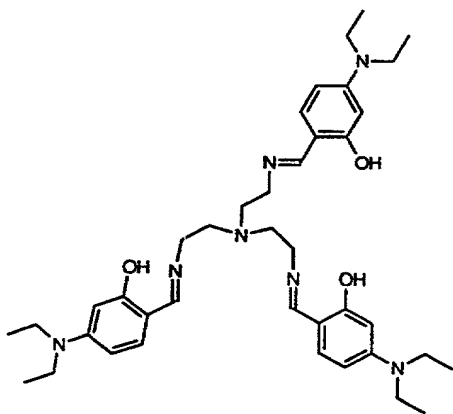
The inventive metal complexes containing a tripodal ligand of the formula (1) also provide an excellent antibacterial effect when used together with peroxygen compounds. The use of the inventive metal complexes containing a tripodal ligand of the formula (1) for killing bacteria or for protecting against bacterial colonization accordingly constitutes a further part of the subject-matter of the present invention.

The examples hereinbelow illustrate the invention without limiting it. Parts and percentages are by weight, unless otherwise stated. The ligands are advantageously prepared under argon.

Example 1: N,N',N''-Tris[salicylideneaminoethyl]amine

527 μl (3.42 mmol) of tris(2-aminoethyl)amine are added dropwise to a clear emulsion of 1.27 g (10.3 mmol) of salicylaldehyde in 90 ml of distilled water at room temperature to form a cloudy yellow suspension, which is subsequently stirred for 20 hours. The precipitate formed is filtered off and dried to constant weight in a vacuum drying cabinet at 35°C. Yield 1.40 g (89%), canary-yellow solid.

^{13}C NMR (CDCl_3): δ = 58.2, 60.3 (NCH_2), 119.1, 120.8, 134.1, 134.2 (tert. aryl-C), 168.4 ($\text{C}=\text{N}$), 120.9, 163.4 (quart. aryl-C).

Example 2: N,N',N''-Tris[4-N-diethylaminosalicylideneaminoethyl]amine

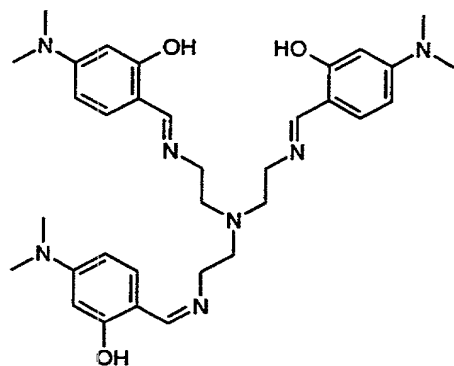
The synthesis is carried out with activated pulverized molecular sieve (3 Å) under argon. To this end, 10.0 g of molecular sieve are ground, heated with a Bunsen burner for 45 min under reduced pressure and cooled down in a stream of argon. 10 g of thusly pretreated molecular sieve and 2.03 g (10.3 mmol) of 4-(N,N-diethylamino)-2-hydroxybenzaldehyde are introduced into 90 ml of toluene at room temperature. The resulting dark red/beige

suspension is admixed with 527 μ l (3.42 mmol) of tris(2-aminoethyl)amine added dropwise. The reaction solution is stirred at room temperature for 25 hours. To work up, the reaction solution is filtered and the filtrate is concentrated under reduced pressure.

Yield 2.34 g (102%), beige/orange solid, still contains ethanol.

^{13}C NMR (CDCl_3): δ = 12.9 ($\text{CH}_2\text{-CH}_3$), 44.5 ($\text{CH}_2\text{-CH}_3$), 54.5, 56.2 (N-CH_2), 98.6, 102.6, 134.2 (tert. aryl-C), 108.3, 151.9, 169.0 (quart. aryl-C), 164.1 (C=N).

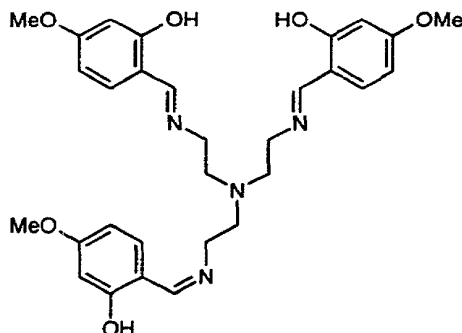
Example 3: N,N',N''-Tris[4-N-dimethylaminosalicylideneaminoethyl]amine



A suspension of 1.70 g (10.3 mmol) of 4-(N,N-dimethylamino)-2-hydroxybenzaldehyde, 527 μ l (3.42 mmol) of tris(2-aminoethyl)amine and 10 g of activated pulverized molecular sieve (3 Å) in 90 ml of absolute toluene is prepared, reacted and worked up as described in Example 2.

Yield: 1.86 g (93%), brownish yellow solid.

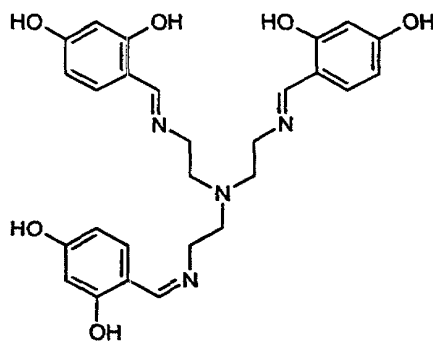
^{13}C NMR (CDCl_3): δ = 40.5 (N-CH_3), 55.5, 56.7 (N-CH_2), 99.8, 103.7, 134.0 (tert. aryl-C), 109.2, 154.6, 168.2 (quart. aryl-C), 164.7 (C=N).

Example 4: N,N',N''-Tris[4-methoxysalicylideneaminoethyl]amine

A suspension of 1.60 g (10.3 mmol) of 2-hydroxy-4-methoxybenzaldehyde, 527 μ l (3.42 mmol) of tris(2-aminoethyl)amine and 10 g of molecular sieve (3 Å) in 90 ml of absolute ethanol is prepared, reacted and worked up as described in Example 2.

Yield: 1.68 g (83%), reddish brown solid.

^{13}C NMR (CDCl_3): δ = 55.7 (OCH_3), 56.1, 56.3 (N-CH_2), 101.7, 106.5, 133.8 (tert. aryl-C), 112.3, 164.4, 167.7 (quart. aryl-C); 165.4 (C=N).

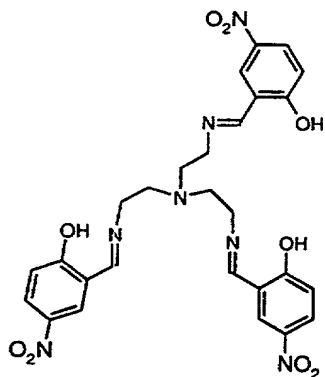
Example 5: N,N',N''-Tris[4-hydroxysalicylideneaminoethyl]amine

A suspension of 1.452 g (10.3 mmol) of 2,4-dihydroxybenzaldehyde in 90 ml of 96% ethanol is reacted with 527 μ l (3.42 mmol) of tris(2-aminoethyl)amine as described in Example 2.

The reaction solution is stirred at room temperature for 8 hours. To work up, the precipitate formed is filtered off and dried to constant weight at 40°C under reduced pressure.

Yield: 1.54g (89%), yellowish orange solid.

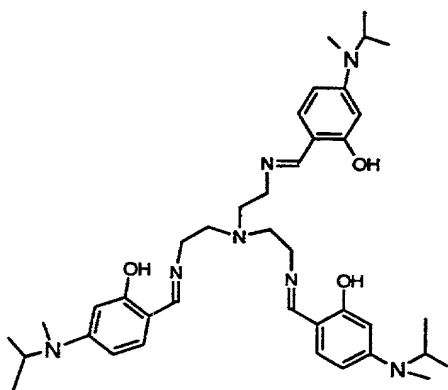
^{13}C NMR (DMSO): δ = 54.9, 55.0 (N-CH_2), 102.7, 106.5, 133.5 (tert. aryl-C), 110.8, 162.1, 166.2 (quart. aryl-C), 164.9 (C=N).

Example 6: N,N',N''-Tris[5-nitrosalicylideneaminoethyl]amine

527 μ l (3.42 mmol) of tris(2-aminoethyl)amine are added dropwise to a suspension of 1.775 g (10.3 mmol) of 2-hydroxy-5-nitrobenzaldehyde in 90 ml of absolute ethanol. After stirring at room temperature for eight hours, the product is filtered off and dried as described in Example 5.

Yield: 1.97 g (97%), yellowish orange solid.

^{13}C NMR (DMSO): δ = 50.2, 52.9 (N-CH₂), 122.3, 128.7, 133.5 (tert. aryl-C.) 167.1 (C=N), 113.3, 132.2, 177.3 (quart. aryl-C).

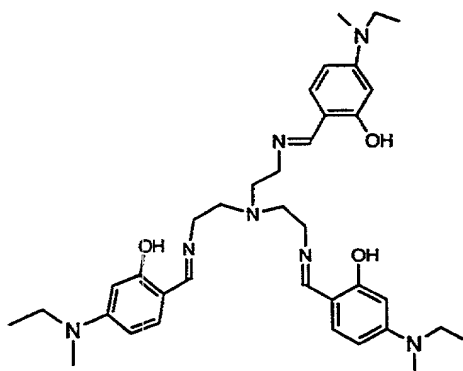
Example 7: N,N',N''-Tris[(4-N-methyl-N-isopropylamino)salicylideneaminoethyl]amine

79.6 μ l (0.52 mmol) of tris(2-aminoethyl)amine are added dropwise to a solution of 0.3 g (1.55 mmol) of 4-(N-isopropyl-N-methylamino)-2-hydroxybenzaldehyde in 14 ml of absolute ethanol at room temperature. The resulting reaction solution is stirred for 8 hours, concentrated, and dried to constant weight at 40°C in a high vacuum.

Yield 352 mg (101%), reddish brown solid, still contains ethanol.

^{13}C NMR (CDCl_3): δ = 21.3 ($\text{NCH}(\text{CH}_3)_2$), 31.4 (NCH_3), 49.9 ($\text{NCH}(\text{CH}_3)_2$), 56.5, 57.9 (NCH_2), 101.3, 105.0, 135.4 (tert. aryl-C), 110.3, 155.5, 169.9 (quart. C), 165.8 ($\text{C}=\text{N}$).

Example 8: N,N',N''-Tris[(4-N-methyl-N-ethylamino)salicylideneaminoethyl]amine

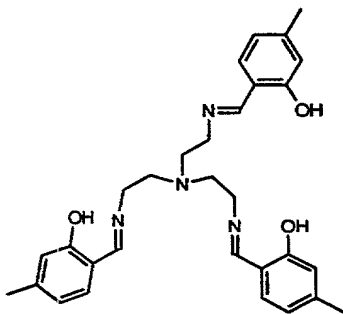


85.6 μl (0.56 mmol) of tris(2-aminoethyl)amine are added dropwise to a solution of 0.3 g (1.55 mmol) of 4-(N-ethyl-N-methylamino)-2-hydroxybenzaldehyde in 15 ml of absolute ethanol at room temperature. The resulting reaction solution is stirred for 2 hours at 50°C , and for a further 8 hours at room temperature. The workup is carried out as described in Example 7.

Yield 310 mg (89%), reddish brown resin.

^{13}C NMR (CDCl_3): δ = 10.6 (NCH_2CH_3), 36.3 (NCH_3), 45.3 (NCH_2CH_3), 53.5, 55.0 (NCH_2), 98.0, 101.7, 132.7 (tert. aryl-C), 107.3, 151.8, 167.4 (quart. aryl-C); 162.9 ($\text{C}=\text{N}$).

Example 9: N,N',N''-Tris[4-methylsalicylideneaminoethyl]amine

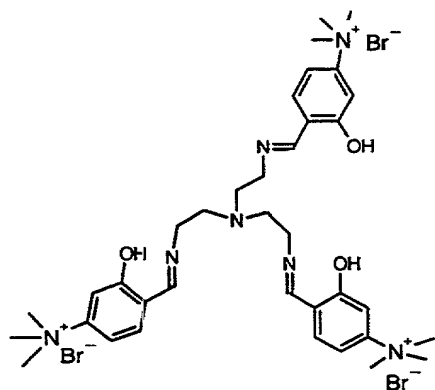


Example 7 is repeated starting with a reaction solution of 0.3 g (2.20 mmol) of 2-hydroxy-4-methylbenzaldehyde and 112.8 μ l (0.73 mmol) of tris(2-aminoethyl)amine in 20 ml of absolute ethanol at room temperature.

Yield: 383 mg (105%), yellow solid, still contains ethanol.

^{13}C NMR (CDCl_3): δ = 22.2 (CH_3), 56.3, 58.2 (NCH_2), 117.6, 119.9, 132.1 (tert. aryl-C), 116.7, 143.2, 161.8 (quart. aryl-C), 166.2 ($\text{C}=\text{N}$).

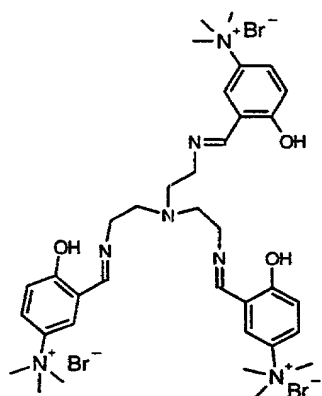
Example 10: N,N',N''-Tris[4-trimethylammoniosalicylideneaminoethyl]amine tribromide



Example 7 is repeated starting with a reaction solution of 0.3 g (1.15 mmol) of 4-formyl-3-hydroxyphenyltrimethylammonium bromide (synthesis method: M. Ando, S. Emoto, Bull. Chem. Soc. Jpn., 42 (9) 2624 (1969)) in 10 ml of absolute ethanol and 59.0 μ l (0.38 mmol) of tris(2-aminoethyl)amine.

Yield: 307 mg (93%), yellow solid.

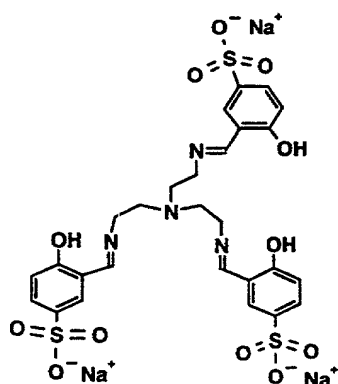
^{13}C NMR (DMSO): δ = 54.3, 54.8 (NCH_2), 56.0 ($-\text{N}^+(\text{CH}_3)_3$), 108.3, 110.3, 133.3 (tert. aryl-C), 118.1, 125.3, 150.3 (quart. aryl-C), 165.0 ($\text{C}=\text{N}$).

Example 11: N,N',N''-Tris[5-trimethylammoniosalicylideneaminoethyl]amine tribromide

Example 7 is repeated starting with a reaction solution of 0.3 g (1.15 mmol) of 3-formyl-4-hydroxyphenyltrimethylammonium bromide [synthesis method: M. Ando, S. Emoto, Bull. Chem. Soc. Jpn., 42 (9) 2624 (1969)] in 10 ml of absolute ethanol and 59.0 μ l (0.38 mmol) of tris(2-aminoethyl)amine.

Yield: 320 mg (97%), orange solid.

^{13}C NMR (DMSO- d_6): δ = 54.3, 55.4 (NCH_2), 56.4 ($\text{N}^+(\text{CH}_3)_3$), 119.0, 123.1, 124.6 (tert. aryl-C), 117.4, 136.5, 164.0, 164.8 (quart. aryl-C), 164.5 ($\text{C}=\text{N}$).

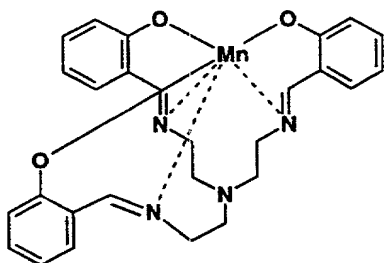
Example 12: N,N',N''-Tris[5-sulfonatosalicylideneaminoethyl]amine, trisodium salt

226 μ l (221.2 mg, 1.482 mmol) of tris(2-aminoethyl)amine are added dropwise to a suspension of 1 g (4.46 mmol) of sodium salicylaldehyde-5-sulfonate in 120 ml of ethanol. After stirring at room temperature for 24 hours, the crude product is filtered off and washed with a little cold ethanol. The crude product is dried in a high vacuum at 35°C.

Yield: 870 mg (77%), lemon yellow solid.

^{13}C NMR (DMSO- d_6): δ = 56.3, 57.7 (N-CH $_2$), 117.8, 130.6, 131.7 (tert. aryl-C), 118.4, 139.5, 163.9 (quart. aryl-C), 167.9 (C=N),

Example 13: Synthesis of the unsubstituted manganese(III) complex



The 1:1 manganese complex is synthesized by reacting 1.50 g (5.6 mmol) of manganese(III) acetate dihydrate with 2.43 g (5.3 mmol) of N,N',N''-tris[salicylideneaminoethyl]amine from Example 1 by the literature method of A. Chakravorty et al. [S.K. Chandra, P. Chakraborty and A. Chakravorty, *J. Chem. Soc., Dalton Trans.* (1993) 863].

Yield: 2.40 g (89%), greenish olive powder.

Elemental analysis $\text{C}_{27}\text{H}_{27}\text{MnN}_4\text{O}_3 \cdot \text{CH}_3\text{OH}$ (542.52)

rec.	62.00	H 5.76	Mn 10.13	N 10.33
------	-------	--------	----------	---------

obs.	62.85	H 5.54	Mn 10.4	N 10.63
------	-------	--------	---------	---------

Alternatively, the manganese(III) complex is synthesized by the literature method of R. Mukherjee et al. [K. Ramesh, D. Bhuniya and R. N. Mukherjee, *J. Chem. Soc., Dalton Trans.* (1991) 2917] by reacting 8.00 g (17.4 mmol) of N,N',N''-tris[salicylideneaminoethyl]amine with 6.41 g (26.2 mmol) of manganese(II) acetate tetrahydrate and subsequent oxidation.

Yield: 7.28 g (76%).

The manganese(III) complexes prepared perform well in DTI screening (see application examples, Table 1).

Application examples:

Example 14: The catalysts were tested for DTI activity. The DTI (dye transfer inhibition) effect a is defined as the following percentage:

$$a = ([Y(E) - Y(A)] / [Y(W) - Y(A)]) * 100$$

where Y(W), Y(A) and Y(E) are the CIE lightnesses of the white material, of the material treated without added catalyst and of the material treated with added catalyst, in that order. $a=0$ characterizes a product of nil utility, the inclusion of which in the wash liquor does nothing to impede dye transfer. $a=100\%$, by contrast, defines a perfect catalyst, which completely suppresses the tainting of the white material.

The test data are determined using the following testing system: 7.5 g of white cotton are treated in 80 ml of wash liquor. This liquor contains the standard detergent ECE phosphate-free (456 IEC) EMPA, Switzerland, in a concentration of 7.5g/l, 8.6 mmol/l H_2O_2 , and a solution of the test dye. The washing process is carried out in a pot in a LINITEST apparatus at 40°C for 30 min.

Commercially available Direct Brown 172 (dye 1) at 10 mg/l of the 250% formulation or Reactive Blue 238 (dye 2) at 6 mg/l of the 100% formulation were used as test dyes. The reflectants spectra of the samples were measured with a SPECTRAFLASH 2000 and transformed into D65/10 lightnesses by the CIE standard procedure.

Table 1 shows the DTI effects a(%) of 1:1 manganese complexes of the ligands of Examples 1-12 and of the manganese complex of Example 13.

The manganese complexes are synthesized either as described in Example 13 or in situ by adding the corresponding manganese(III) salt in ethanolic solution. The complexes are always used at 20 $\mu\text{mol/l}$ wash liquor. It is evident from the table that the recited catalysts are very effective DTI catalysts.

Table 1

Manganese complex of ligand of example	DTI effect a(%)	
	Dye 1	Dye 2
1 (by in situ method)	91	96
2	78	73
3	85	80
4	83	67

5	78	27
6	70	80
7	84	83
8	85	81
9	87	94
10	90	96
11	86	94
12	80	99
13 (isolated manganese complex of ligand of Example 1)	99	95

Example 15: Table 2 shows that the manganese complex of the ligand of Example 1 is very effective in inhibiting the redeposition of dyes of various classes. The experimental conditions are described in Example 14. The use concentration of the catalyst is 10 $\mu\text{mol/l}$.

Table 2

Test dye	Dye concentration mg/l	DTI effect [a (%)]
Direct Brown 172 250%	10	79
Reactive Blue 238 100%	6	98
Reactive Black 005 133%	12	54
Reactive Black 022 400%	6	73
Reactive Blue 019 special 100%	20	85
Acid Blue 113 180%	6	98
Disperse Violet 001 100%	6	79

Example 16: The ligands of the invention enhance the bleaching effect of hydrogen peroxide in wash liquors significantly. The bleach tests are carried out as follows: 7.5 g of white cotton fabric and 2.5 g of a tea stain on cotton fabric are treated in 80 ml of wash liquor. This liquor

contains the standard laundry detergent ECE phosphate-free (456 IEC) EMPA, Switzerland in a concentration of 7.5 g/l, hydrogen peroxides in a concentration of 8.6 mmol/l and optionally 100 $\mu\text{mol/l}$ of one of the ligands according to the invention. The washing process takes place in a steel pot in a LINITEST apparatus at 40°C for 30 minutes. The bleaching results are evaluated using the increase in lightness DY (lightness difference as per CIE) of the stain due to the treatment.

Table 3 contains the DY values for the systems tested.

Table 3

DY with H_2O_2 only	DY with H_2O_2 and ligand of Example 2	DY with H_2O_2 and ligand of Example 3	DY with H_2O_2 and ligand of Example 7	DY with H_2O_2 and ligand of Example 8
18	21	22	21	22

Example 17: The manganese complex of the ligand of Example 1 is associated with a level of damage on coloured laundry that is acceptable. With regard to dye damage, less degradation is observed than with the TAED-activated bleaching system, even with regard to dyes known to be very sensitive. The TAED-activated bleaching system is considered to be the best oxygen bleaching technology has to offer, and its damage/benefit ratio is accepted. Use as described above gives the following percentage dye loss after fivefold treatment.

Table 4

Test dyeing	Dye loss %	
	Catalyst 50 $\mu\text{mol/l}$	TAED
Vat Brown 001	5	5
Reactive Brown 017	5	15
Reactive Red 123	5	10
Direct Blue 085	15	15
Vat Blue 004	0	5
Reactive Black 005	15	25

Example 18: The manganese complex of the ligand of Example 1 is similar with regard to fibre damage on dyed materials to the cited TAED system. Use as described above gives the following relative DP reduction after fivefold treatment.

Table 5

Test dyeing	relative DP reduction %	
	Catalyst 50 µmol/l	TAED
Reactive Brown 017	15	15
Vat Brown 001	5	5
Reactive Red 123	5	0
Direct Blue 085	10	5
Vat Blue 004	5	0
Reactive Black 005	5	5

Example 19: Providing a liquid preparation

20 g of the catalyst of Example 13, 4 g of a nonionic dispersant (block polymers of ethylene oxide and propylene oxide, tradename: Pluronic F108), 176 g of deionized water and 400 g of glass beads (\varnothing 0.5 mm) are stirred at 850 rpm in a grinding pot at 20°C for 3 hours. The glass beads are then filtered off. A liquid preparation of the catalyst is obtained.

Example 20: Providing a solid preparation

0.1 g of the catalyst of Example 13 and 0.9 g of anhydrous sodium sulfate were thoroughly trituated using a mortar and pestle.

Example 21: Use example for solid and liquid preparations

The liquid and solid preparations of Examples 19 and 20 were tested for their DTI effect a(%) (see Example 14). The test data are determined using the testing system of Example 14, except that this time 0.25 g of a piece of cotton dyed with the dye Direct Black

22 (EMPA, Switzerland) is used as dye donor. The catalyst concentration in the wash liquor is always 50 μmol . In the experiments, the catalyst is added to the testing system in five different forms: i) as a solid without further treatment, ii) in the form of a concentrated solution in DMF, iii) in the form of the suspension of Example 19, iv) in the form of the solid preparation of Example 20, v) 1.7 g of the suspension of Example 19 is thoroughly mixed with 48.3 g of laundry detergent (IEC 456 Type A) and 40 g of water in a grinding dish and dried at room temperature under reduced pressure for 50 hours. The laundry detergent thus formed is then classified, and the 315-800 μm fraction is used for the washing test. This test is carried out with 7.5 g/l of this laundry detergent instead of 7.5 g/l of the standard laundry detergent (IEC 456 Type A).

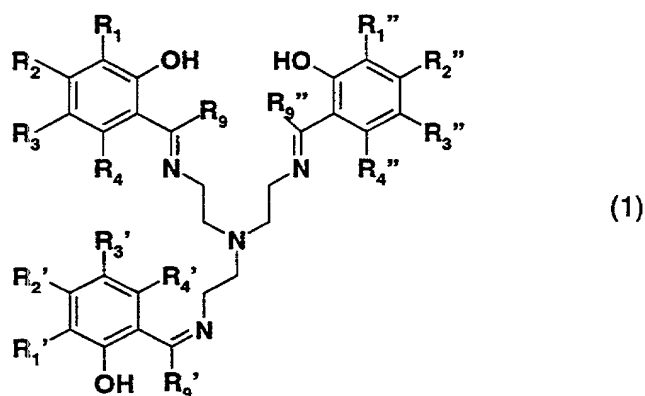
Table 6 shows the DTI effects a(%). The table shows that the solid preparation, the suspension and the suspension incorporated into the laundry detergent all provide superior DTI effects than the untreated, solid catalyst and than the dissolved catalyst.

Table

Catalyst system	DTI effect a(%)
i) Catalyst is solid	49
ii) Catalyst dissolved in DMF	0
iii) Catalyst triturated with Na_2SO_4	75
iv) Catalyst suspension	71
v) Catalyst suspension incorporated into laundry detergent	83

What is claimed is:

1. The use of metal complexes containing a tripodal ligand of the formula

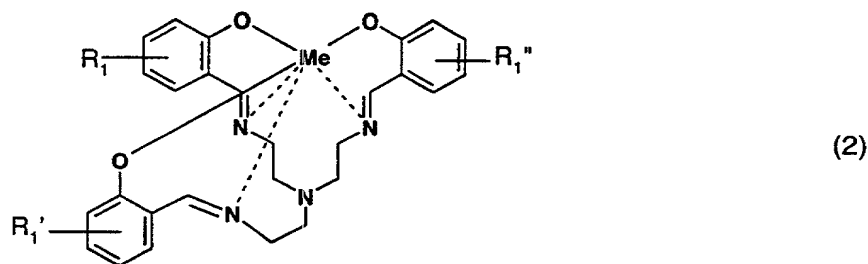


where

R_1 , R_2 , R_3 , R_4 , R_1' , R_2' , R_3' , R_4' , R_1'' , R_2'' , R_3'' and R_4'' are each independently hydrogen, cyano, halogen, SO_3M , where M is hydrogen, an alkali metal cation, an alkaline earth metal cation, ammonium or an organic ammonium cation, SO_2NH_2 , SO_2NHR_5 , $\text{SO}_2\text{N}(\text{R}_5)_2$, OR_5 or COOR_5 , where R_5 is hydrogen or linear or branched C_1 - C_4 alkyl, nitro, linear or branched C_1 - C_8 alkyl, linear or branched fluorinated or perfluorinated C_1 - C_8 alkyl, NHR_6 , NR_6R_7 , $\text{N}^+\text{R}_6\text{R}_7\text{R}_{10}$ or linear or branched C_1 - C_8 alkyl- R_8 , where R_8 is OR_5 , COOR_5 , NH_2 , NHR_6 , NR_6R_7 or $\text{N}^+\text{R}_6\text{R}_7\text{R}_{10}$, where R_6 , R_7 and R_{10} are identical or different and each is linear or branched C_1 - C_{12} alkyl or where R_6 and R_7 combine with the joining nitrogen atom to form a 5-, 6- or 7-membered ring, which may contain further heteroatoms, and where R_9 , R_9' and R_9'' are each independently hydrogen, linear or branched C_1 - C_8 alkyl or aryl, as catalysts for oxidations with peroxygen compounds.

2. The use according to claim 1, wherefor the metal complex is an Mn(III) and Fe(III) complex containing a ligand of the above formula (1), especially an Mn(III) and Fe(III) complex which contains a ligand of the above formula (1) and metal in a molar ratio of 1:1.

3. The use of the 1:1 metal(III) complexes of the formula



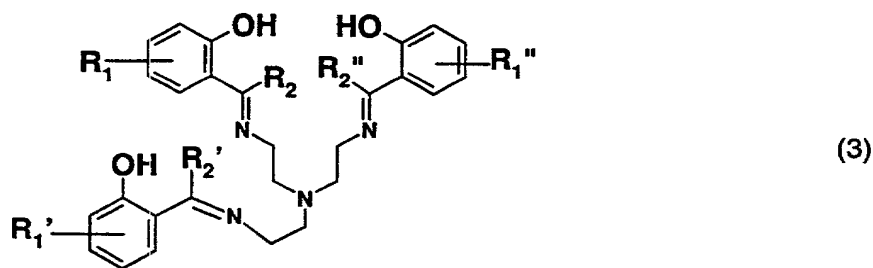
where Me is Mn or Fe, R_1 , R_1' and R_1'' are each independently hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxyl, nitro, NHR_6 , NR_6R_7 or $-N^+R_5R_6R_7$, where R_5 , R_6 and R_7 are each independently C_1 - C_4 alkyl, as catalysts for oxidations with peroxygen compounds.

4. The use according to claim 3, wherefor the metal complex is an Mn(III) complex.

5. The use of the metal complexes according to claim 1, containing a tripodal ligand of the formula (1), in aqueous solution together with peroxygen compounds for bleaching spots or stains on textile material or for preventing the redeposition of migrating dyes as part of a washing process, or for cleaning hard surfaces, especially crockery or glass.

6. The use of the tripodal ligand of the formula (1) according to claim 1 in aqueous solution together with peroxygen compounds for bleaching spots or stains on textile material.

7. The use according to any one of claims 1 to 6, wherefor the tripodal ligand conforms to the formula



where

R_1 , R_1' and R_1'' are each independently hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxyl, nitro, NHR_6 , NR_6R_7 or $N^+R_5R_6R_7$, where R_5 , R_6 and R_7 are each independently C_1 - C_4 alkyl and R_2 , R_2' and R_2'' are each independently hydrogen, linear or branched C_1 - C_8 alkyl or aryl.

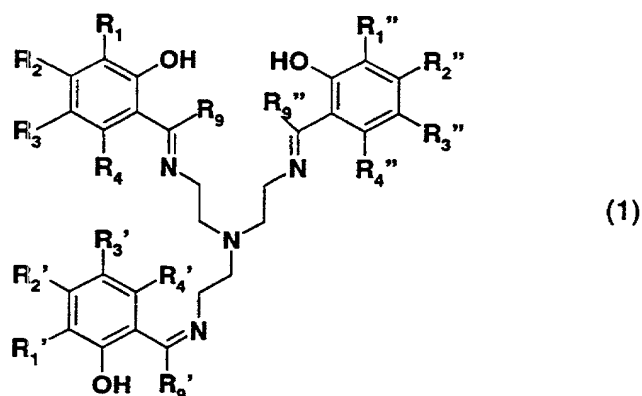
8. A manganese(III) or iron(III) complex containing a tripodal ligand of the formula



where

$R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3''$ and R_4'' are each independently hydrogen, cyano, halogen, SO_3M , where M is hydrogen, an alkali metal cation, an alkaline earth metal cation, ammonium or an organic ammonium cation, SO_2NH_2 , SO_2NHR_5 , $SO_2N(R_5)_2$, OR_5 or $COOR_5$, where R_5 is hydrogen or linear or branched C_1 - C_4 alkyl, nitro, linear or branched C_1 - C_8 alkyl, linear or branched fluorinated or perfluorinated C_1 - C_8 alkyl, NHR_6 , NR_6R_7 , $N^{\oplus}R_6R_7R_{10}$ or linear or branched C_1 - C_8 alkyl- R_8 , where R_8 is OR_5 , $COOR_5$, NH_2 , NHR_6 , NR_6R_7 or $N^{\oplus}R_6R_7R_{10}$, where R_6 , R_7 and R_{10} are identical or different and each is linear or branched C_1 - C_{12} alkyl or where R_6 and R_7 combine with the joining nitrogen atom to form a 5-, 6- or 7-membered ring, which may contain further heteroatoms, and where R_9 , R_9' and R_9'' are each independently hydrogen, linear or branched C_1 - C_8 alkyl or aryl, subject to the condition that in the manganese(III) complex at least one of the substituents $R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3'', R_4'', R_9, R_9'$ and R_9'' has a meaning other than hydrogen and that at least one of the substituents R_3, R_3' and R_3'' has a meaning other than chlorine when the substituents $R_1, R_2, R_4, R_1', R_2', R_4', R_1'', R_2'', R_4'', R_9, R_9'$ and R_9'' are all hydrogen.

9. A ligand of the formula



where

$R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3''$ and R_4'' are each independently hydrogen, cyano, halogen, SO_3M , where M is hydrogen, an alkali metal cation, an alkaline earth metal cation, ammonium or an organic ammonium cation, SO_2NH_2 , SO_2NHR_5 , $SO_2N(R_5)_2$, OR_5 or $COOR_5$, where R_5 is hydrogen or linear or branched C_1 - C_4 alkyl, nitro, linear or branched C_1 - C_8 alkyl, linear or branched fluorinated or perfluorinated C_1 - C_8 alkyl, NHR_6 , NR_6R_7 , $N^+R_6R_7R_{10}$ or linear or branched C_1 - C_8 alkyl- R_8 , where R_8 is OR_5 , $COOR_5$, NH_2 , NHR_6 , NR_6R_7 or $N^+R_6R_7R_{10}$, where R_6, R_7 and R_{10} are identical or different and each is linear or branched C_1 - C_{12} alkyl and where R_6 and R_7 combine with the joining nitrogen atom to form a 5-, 6- or 7-membered ring, which may contain further heteroatoms, or where R_9, R_9' and R_9'' are each independently hydrogen, linear or branched C_1 - C_8 alkyl or aryl, subject to the condition that at least one of the substituents $R_1, R_2, R_3, R_4, R_1', R_2', R_3', R_4', R_1'', R_2'', R_3'', R_4'', R_9, R_9'$ and R_9'' has a meaning other than hydrogen and that at least one of the substituents R_3, R_3' and R_3'' has a meaning other than chlorine when the substituents $R_1, R_2, R_4, R_1', R_2', R_4', R_1'', R_2'', R_4'', R_9, R_9'$ and R_9'' are all hydrogen.

10. A washing or cleaning process, which comprises adding to the liquor, which contains a peroxidic detergent, 0.1 to 200 μmol per litre of wash liquor of one or more metal complexes containing a tripodal ligand of the formula (1) or an uncomplexed ligand of the formula (1).

11. A process for preventing the redeposition of migrating dyes in a wash liquor, which comprises adding to the wash liquor, which contains a peroxidic detergent, 0.5 to 150, preferably 1.5 to 75, especially 7.5 to 40, mg per litre of wash liquor of one or more metal complexes containing a tripodal ligand of the formula (1).

12. A laundry detergent comprising

- I) 5 - 90%, preferably 5 - 70%, of A) an anionic surfactant and/or B) a nonionic surfactant,
- II) 5 - 70%, preferably 5 - 50%, especially 5 - 40%, of C) a builder,
- III) 0.1 - 30%, preferably 1 - 12%, of D) a peroxide, and
- IV) 0.005 - 2%, preferably 0.02 - 1%, especially 0.1 - 0.5%, of E) a metal complex containing a tripodal ligand of the above-defined formula (1), the percentages all being percent by weight based on the total weight of the laundry detergent.

13. The use of metal complexes containing a tripodal ligand of the formula (1) as catalysts for reactions with peroxygen compounds in cleaning solutions for hard surfaces, especially for crockery.

14. A hard surface cleaner, especially a cleaner for crockery, preferably a crockery cleaner for use in machine cleaning processes, comprising a metal complex containing a tripodal ligand of the formula (1) according to claim 1 as a bleach catalyst.

15. The process for cleaning hard surfaces, especially crockery, using a cleaner according to claim 14.

16. The use of metal complexes containing a tripodal ligand of the formula (1) according to claim 1 as catalysts for reactions with peroxygen compounds in cleaning solutions for tiles and inter-tile joints.

17. The use of the metal complexes according to claim 1, containing a tripodal ligand of the formula (1), for killing bacteria or for protecting against bacterial colonization.

18. An aqueous suspension comprising

- 1 - 60% by weight, preferably 5 - 30% by weight, of a metal complex containing a tripodal ligand of the formula (1) according to claim 1,
- a) 0.5 to 15% by weight, preferably 1 - 5% by weight, of a dispersant,
- b) 0 - 10% by weight of a further ingredient, and
- c) 15 - 98.5% by weight of water.

19. A solid preparation comprising

- a) 1 - 99% by weight, preferably 5 - 50% by weight, of a metal complex containing a tripodal ligand of the formula (1) according to claim 1,
- b) 1 to 99% by weight, preferably 50 - 95% by weight, of a carrier material,
- c) 0 - 20% by weight of a dispersant,
- d) 0 - 10% by weight of a further ingredient, and
- e) 0 - 5% by weight of water.

20. An aqueous suspension or solid preparation according to either of claims 18 and 19, comprising a metal complex containing a tripodal ligand of the formula (1) according to claim 1 with an average particle size of less than 20 μm , especially between 0.1 and 15 μm .

21. The use of metal complexes containing a tripodal ligand of the formula (1) according to claim 1 as catalysts for reactions with peroxygen compounds for removing printing inks from printed waste paper (de-inking).

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATIONS

☒ Original ☐ Supplemental ☐ Substitute ☒ PCT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if more than one name is listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Metal complexes of tripodal ligands

which is described and claimed in:

- ☐ the attached specification.
- ☐ the specification in U.S. Application No. _____
filed _____, and as amended on _____ (if applicable).
(day/month/year) (day/month/year)
- ☒ the specification in International Application No. **PCT/EP 00/06420**
filed **06/07/00**
(day/month/year)
assigned U.S. Application No. _____ (if applicable), and as amended
- ☐ under PCT Article 19 on _____ (if applicable)
(day/month/year)
- ☐ under PCT Article 34 on _____ (if applicable)
(day/month/year)
- ☐ and further amended on _____ (if applicable)
(day/month/year)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information which is known by me to be material to the patentability of this application as defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America relating to this subject matter having a filing date before that of the application on which priority is claimed:

COUNTRY/REGION (OR PCT)	APPLICATION No.	FILING DATE (day/month/year)	PRIORITY CLAIMED
----------------------------	-----------------	---------------------------------	------------------

Europe (designating DE)	99810631.4	14/07/99	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No <input type="checkbox"/> Yes <input type="checkbox"/> No <input type="checkbox"/> Yes <input type="checkbox"/> No <input type="checkbox"/> Yes <input type="checkbox"/> No <input type="checkbox"/> Yes <input type="checkbox"/> No
----------------------------	------------	----------	---

I hereby claim the benefit under 35 U.S.C. § 119 (e) of any United States provisional application(s) listed below:

APPLICATION NO.	FILING DATE (day/month/year)
-----------------	---------------------------------

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or PCT international application(s) designating the United States listed below and, insofar as the application discloses and claims subject matter in addition to that disclosed in the prior copending application, I acknowledge the duty to disclose all information known by me to be material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. APPLICATION No.	FILING DATE (day/month/year)	STATUS		
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned

PCT APPLICATION No. (designating the U.S.)	INTERNATIONAL FILING DATE (day/month/year)	U.S. APPLICATION No. (if any)	STATUS
			<input type="checkbox"/> Patented <input type="checkbox"/> Pending <input type="checkbox"/> Abandoned

I hereby appoint the following attorneys and agents, associated with Customer No. 000324, each of them with full power of substitution, revocation and appointment of associates, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

6
Luther A. R. Hall (Reg. No. 27,337), JoAnn L. Villamizar (Reg. No. 30,598), Kevin T. Mansfield (Reg. No. 31,635), David R. Crichton (Reg. No. 37,300), Michele A. Kovaleski (Reg. No. 37,865) and Tyler A. Stevenson (Reg. No. 46,388).

Address all correspondence associated with Customer No. 000324 to **Ciba Specialty Chemicals Corporation, Patent Department, 540 White Plains Road, P.O. Box 2005, Tarrytown, NY 10591-9005.**

10031999-011002
100
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole
or first joint inventor Frank BACHMANN

Inventor's signature Frank Bachmann Date 03.12.07
(day/month/year)

Residence Lehener Strasse 148
79106 Freiburg
Germany

DEX

Citizenship German

Post Office Address same as above

2-00

Full name of second joint inventor, if any Josef DANNACHER

Inventor's signature J. Dannacher Date 5-12-01
(day/month/year)

Residence Peter Ochs-Strasse 33
4059 Basel CHX
Switzerland

Citizenship Swiss

Post Office Address same as above

3-00
2003199-011002

Full name of third joint inventor, if any Menno HAZENKAMP

Inventor's signature M. Hazenkamp Date 5.12.01
(day/month/year)

Residence Obere Weid 10
4125 Riehen CHX
Switzerland

Citizenship Dutch

Post Office Address same as above

4-00

Full name of fourth joint inventor, if any Gunther SCHLINGLOFF

Inventor's signature Gunther Schlingloff Date 3.12.01
(day/month/year)

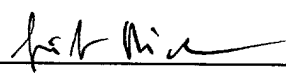
Residence Dinkelbergstrasse 64
4125 Riehen CHX
Switzerland

Citizenship Swiss

Post Office Address same as above

5-00

Full name of fifth
joint inventor, if any Grit RICHTER

Inventor's signature  Date 5-12-2001
(day/month/year)

Residence **Erasmusstrasse 2**
79395 Neuenburg
Germany DEX

Citizenship **German**

Post Office Address same as above

6-00
30031999-031000

Full name of sixth
joint inventor, if any Helena DBALY

Inventor's signature  Date 3.12.2001
(day/month/year)


Residence **Stettbrunnenweg 92**
4132 MuttENZ
Switzerland CHX

Citizenship **Swiss**

Post Office Address same as above

7-00

Full name of seventh
joint inventor, if any Rainer Hans TRABER

Inventor's signature  Date 3.12.01
(day/month/year)

Residence **Im Stockacker 26**
4153 Reinach
Switzerland CHX

Citizenship **German**

Post Office Address same as above